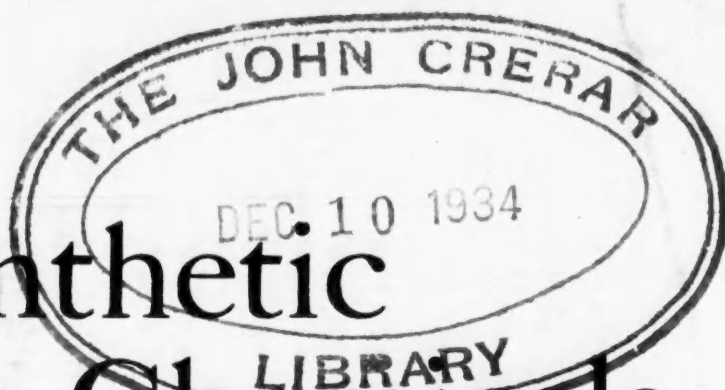


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# Synthetic Organic Chemicals

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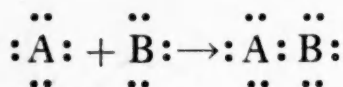
DECEMBER, 1934

No. 2

## Co-ordinate Valence in Organic Chemistry

IN THE October issue of SYNTHETIC ORGANIC CHEMICALS, there appeared a short discussion, "Types of Valence," wherein electrovalence, covalence, and co-ordinate valence were defined and illustrated with some notes on the properties of the first two.

In 1916, G. N. Lewis postulated the formation of a valence where both electrons are contributed by the same atom. This may be expressed schematically thus:



so that each atom has now an octet.

Sidgwick calls such a linkage a co-ordinate valence, since it affords an explanation of Werner's co-ordination compounds, and represents it  $A \rightarrow B$ . He suggested the term, "donor" for the atom supplying the electrons for the union (A, above) and for the other atom (B) the term, "acceptor."

Sugden suggested that it be called a semi-polar double bond, emphasizing that it would be written as a double bond in the usual formulae of organic chemistry, and that a certain electrical moment is set up by the redistribution of electrons between previously neutral atoms. Lowry's representations are also used:  $A \rightleftharpoons B$  or  $A^+ - B^-$ .

One of the most useful tools in the detection and interpretation of co-

ordinate valencies is Sugden's parachor. This is a measure of the molecular volume of a liquid at constant surface tension, and is defined by the equation,

$$(P) = \frac{M\gamma^{1/4}}{D-d},$$

where M,  $\gamma$ , D, and d are respectively molecular weight, surface tension, density of the liquid, and density of the vapor.

By determining the parachors of a great many sets of isomers and compounds differing from one another by known quantities, it was found that the parachor is an additive property; thus, values were found for the common elements and linkages of organic chemistry. For example, one carbon atom adds 4.8 units to the parachor of a compound, hydrogen 17.1, a double bond 23.2, and the presence of a six-membered ring 6.1 units. A single bond makes no contribution.

From this, it is possible to predict the parachor of a compound from its structural formula, or conversely, to choose between formulae involving different types of linkage.

Upon examination of a large number of doubly linked compounds, it was found that many gave the predicted parachor value, and many did not. Instead of a value of 23.2 for what the usual formulae indicate as a double bond, a value averaging -1.6 was

found, showing clearly that there are two types of "double" bonds. The co-ordinate valence, or semi-polar double bond, has nearly the same parachor effect as a single bond—the slight negative value is presumably due to electrostatic attraction.

This was excellent verification of the existence of such compounds, which Lewis had predicted.

Some of the more common groupings, with their formulae in the light of the above, are shown.

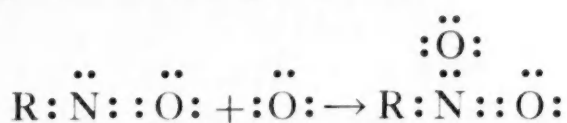
Non-polar or covalent:

Organic carbonates	$(RO)_2C=O$
Nitroso compounds	$R-N=O$
Organic nitrites	$R-O-N=O$
Carbon disulphide	$S=C=S$

Semi-polar double bonds, or co-ordinate valency:

Nitro compounds	$R-\overset{\overset{O}{\parallel}}{N}\rightarrow O$
Alkyl nitrates	$R-O-\overset{\overset{O}{\parallel}}{N}\rightarrow O$
Azoxy compounds	$R-\overset{\overset{O}{\parallel}}{N}=N-R$ $\downarrow$ $O$
Dimethyl sulphate	$(MeO)_2S\rightarrow O$ $\downarrow$ $O$
Organic phosphates	$(RO)_3P\rightarrow O$
Thionyl chloride	$Cl_2S\rightarrow O$
Ethyl sulphite	$(EtO)_2S\rightarrow O$
Phosphorous oxychloride	$Cl_3P\rightarrow O$

For example, the nitrogen of a nitroso group has a complete octet, but has a "lone pair" of unshared electrons. When this is oxidized to a nitro compound, these two electrons are shared with an oxygen, completing its octet:



Another evidence for the existence of co-ordinate valence is found in stereochemical considerations. A number of optically active organic compounds of sulphur of the type  $XY S \rightarrow Z$  have been prepared. The formula shown is satisfactory, but, if they be represented  $XY S=Z$ , a plane of symmetry can be shown in a space model.

Similarly, the amine oxides, which can give rise to optical activity, are represented as having the oxygen attached by a co-ordinate linkage, as  $R_3N \rightarrow O$ .

As pointed out before, the formation of a co-ordinate valence sets up a dipole. This increases the dielectric constant, and, due to intermolecular attraction, makes the compound less volatile. This explains the great difference in boiling point between nitro compounds and the isomeric nitrites.

Chelate compounds, discussed earlier in this series of articles (S.O.C., July, 1934) represent a special case of co-ordinate valency, wherein a ring is formed by the union of a donor and an acceptor in the same molecule. The metallic derivatives of  $\beta$ -diketones and the mordanted dyes are the most outstanding examples.

Co-ordinate valencies can be formed through hydrogen, as in the association of water and alcohols, and certain hydrogen chelate compounds.

In Werner's co-ordination compounds, many chelate compounds,  $SF_6$ ,  $OsF_8$ , and similar compounds, and co-ordinated hydrogen, the octet rule is incompatible with the representation of each valence as a sharing of two electrons. Either there are more than eight electrons shared in the outer shell of the metals (more than two in the case of hydrogen) or at least some of the bonds must be links of single electrons. Various explanations are given by Sidgwick, Lewis, and Sugden.

## Temperature Regulator

THE following is a description of a very flexible temperature regulator for a water bath. It can be constructed with ordinary materials, yet it maintains surprisingly even temperatures.

The regulator proper can be placed in any convenient vessel. The accompanying photograph, Figure 1, shows it assembled in a 20-gallon earthenware crock equipped with a motor-driven stirrer and constant-level regulator.

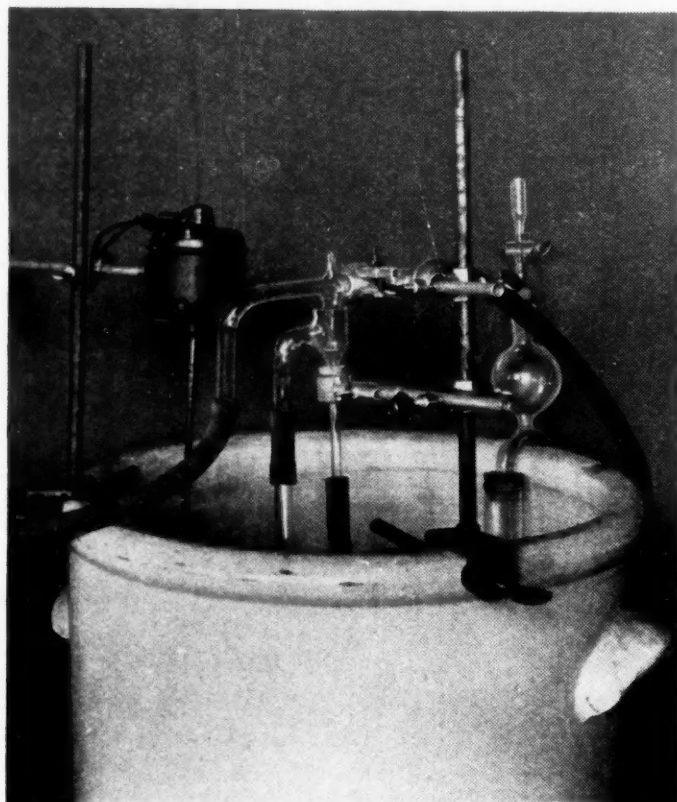


FIGURE 1

The diagram, Figure 2, depicts how easily the regulator can be constructed and adapted to high or low temperatures.

The regulator consists of a glass container, G, partially filled with mercury, H; a liquid, X, which boils about 5° to 10° C. above the desired bath temperature; and an air space, O. As the vapor pressure of the liquid increases, it forces mercury out of the container, G, and through the pressure tubing connection, F, up to the shut-off, E. Water entering through A will be diverted through C or

B depending upon the position of the mercury at E. D is an opening in the glass tube which prevents siphoning in A to B or E. The sensitivity of the regulator and desired temperature may be controlled by the size of G, the vapor pressure of the liquid X, the amount of the gas phase in container G, the length of the mercury column to E, etc., and by raising or lowering the tube at the shut-off, E.

In higher temperature water baths heated by electrical or other means, the desired temperature is maintained by running cold water in through A, Figure 2, and to the bath through B

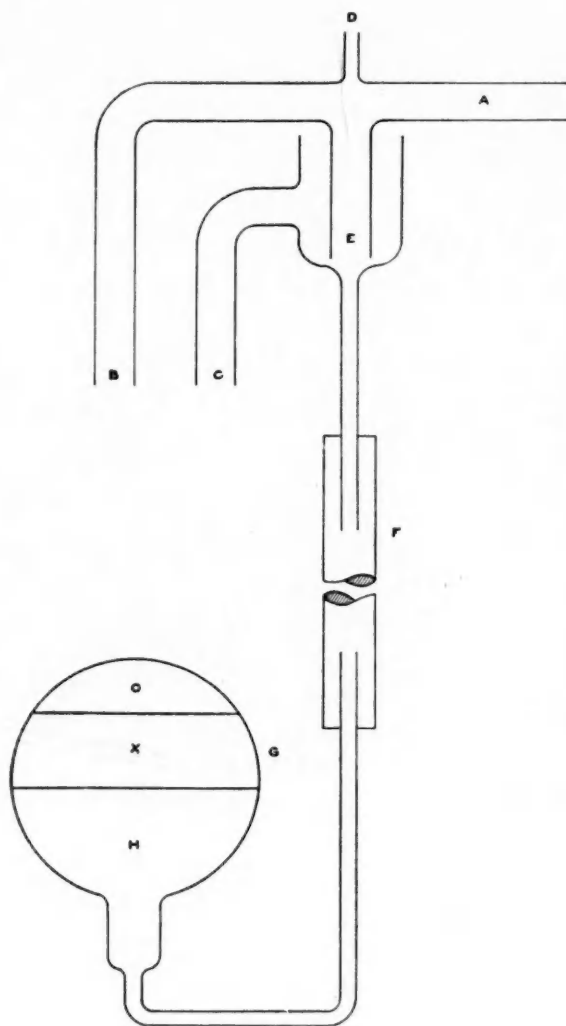


FIGURE 2

If the temperature falls below the desired value, the cooling water will be exhausted to a drain through C. As soon



as the temperature rises to the desired point, the regulator, if properly adjusted so that the mercury will shut off the flow at E, passes the incoming cold water through B to the bath. When equilibrium has been attained, a portion of the cold water will flow through both C and B, thus maintaining the bath at the desired temperature.

When desired, low bath temperatures may be maintained by running hot water in at A and to the bath through C. As the temperature rises, the mercury will diminish the flow of hot water

at E, diverting the excess through B.

To maintain a bath below room temperature, cold water is passed into the regulator at A and allowed to flow into the bath through B. If the temperature falls below the desired value, the lowering of the mercury column at E will allow the cold water to flow through C to the drain.

When the regulator has been set up in the bath and surrounded with water at the desired temperature, the final adjustment is made by slightly raising or lowering the tube E.

## Eastman Organic Reagents for Metals (xxxv)

### $\alpha$ -NAPHTHYLAMINE AND SULFANILIC ACID

Doisy and Bell, J. BIOL. CHEM. 45, 313 (1920-21)

Sodium in blood may be determined colorimetrically through the complex sodium caesium bismuth nitrite. The sample is wet-ashed or first deproteinized and then ashed. After removal of iron and phosphates with potassium carbonate in the presence of bismuth nitrate, the solution is acidified with nitric acid, cooled, and 3 cc. of the precipitating reagent added per milligram of sodium. In the preparation of the reagent, a solution of 3 grams of bismuth nitrate is added to 30 grams of potassium nitrite in 60 cc. of water, a solution of 1.6 grams of caesium nitrate and 1 cc. 2N nitric acid added and the solution diluted to 100 cc.

After standing 24 hours at room temperature in H<sub>2</sub>S-free illuminating gas, the precipitate formed in the test solution is filtered and washed rapidly with 50% acetone saturated with sodium bismuth caesium nitrite. To the precipitate in a beaker, 10 cc. of a 10% solution of potassium hydroxide and tartaric acid are added, warmed, and the

solution diluted to 100 cc. An aliquot portion containing 0.01 mg. of nitrogen is diluted to 90 cc., 2 cc. each of 0.8% sulfanilic acid in 5N acetic acid, and 0.5%  $\alpha$ -naphthylamine in 5N acetic acid added, and the solution diluted to 100 cc. After standing for 20 minutes, the color is compared to a standard prepared in the same manner from silver nitrite and sodium chloride.

### 8-HYDROXYQUINOLINE SULFATE

N. Schoorl, PHARM. WEEKBLAD 56, 325 (1919)

Barium and arsenic can be determined qualitatively through the precipitate formed with 8-hydroxyquinoline sulfate. To an aqueous solution suspected of containing arsenic or barium is added 0.1% of 8-hydroxyquinoline sulfate and the mixture is allowed to stand overnight. Pentavalent arsenic forms long needles soluble in hydrochloric acid, nitric acid, and ammonium hydroxide. Barium appears as a white microcrystalline precipitate insoluble in these same reagents. The barium crystals can be readily distinguished microscopically from lead, strontium, silver, and copper.